



Co-pyrolysis of Chinese lignite and biomass in a vacuum reactor



Xiao Yang, Chengyong Yuan, Jiao Xu^{*}, Weijiang Zhang

School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, PR China

HIGHLIGHTS

- Vacuum reactor, high temperature and low heating rate were employed for co-pyrolysis.
- Product yields, char structure, gas and tar compositions were studied.
- Remarkable synergetic effects were observed.
- Potential explanations for synergetic effects were discussed.

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ABSTRACT

A vacuum fixed bed reactor was applied to pyrolyze lignite, biomass (rice husk) and their blend with high temperature (900 °C) and low heating rate (10 °C/min). Pyrolytic products were kept in the vacuum reactor during the whole pyrolysis process, guaranteeing a long contact time (more than 2 h) for their interactions. Remarkable synergetic effects were observed. Addition of biomass obviously influenced the tar and char yields, gas volume yield, gas composition, char structure and tar composition during co-pyrolysis. It was highly possible that char gasification, gaseous phase interactions, and secondary tar cracking were facilitated when lignite and biomass were co-pyrolyzed.

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1. Introduction

Recently, co-utilization of low rank coal (lignite) and renewable fuels has received increasing attention for economic and environmental advantages. Particularly, in China, that is an urgent demand. China has abundant lignite, while, unfortunately, it's not suitable to use lignite directly because of its low energy quality (high moisture content and low heating value) and negative contributions to environment (pollutants and CO₂ emission). Co-processing lignite with biomass which is renewable and environmentally friendly can solve this problem to a large extent.

Co-pyrolysis is one of the promising methods. Many studies have carried out pyrolysis of lignite/biomass blends to examine the existence of synergetic effects. Generally, biomass, as the hydrogen-donor during co-pyrolysis, can rapidly release much more volatiles (such as CO, CO₂, H₂O and H₂) which may promote "gas–lignite" interactions, char gasification, secondary tar cracking and gaseous phase interactions, leading to variations in reaction

kinetics, product distributions, tar and gas compositions (Li et al., 2013; Weiland et al., 2012; Sonobe et al., 2008; Zhang et al., 2007; Vuthaluru, 2004). Besides, the present of alkali and alkaline earth metals (AAEM) in biomass can invite a catalytic effect, facilitating those interactions in further (Vassilev et al., 2010; Keown et al., 2008; Veraa and Bell, 1978).

However, the findings, not as expected, were controversial. Some researchers observed synergies in products' yields and compositions of tar and gas (Li et al., 2014; Kerkkaiwan et al., 2013; Haykiri-Acma and Yaman, 2010; Park et al., 2010), while others reported the lack of synergistic effects during co-pyrolysis (Aboyade et al., 2013; Idris et al., 2010; Sadhukhan et al., 2008; Meesri and Moghtaderi, 2002). The differences of pyrolysis conditions (temperature, heating rate, pressure, contact time, etc.), reactor types and fuel types employed in those studies might determine whether synergy effects were observed.

In this work, a vacuum fixed bed reactor was applied to pyrolyze lignite, biomass (rice husk) and their blend with high temperature (900 °C) and low heating rate (10 °C/min). Pyrolytic products were kept in the vacuum reactor during the whole pyrolysis process, guaranteeing a long contact time that reported

^{*} Corresponding author. Tel.: +86 22 27402028.

E-mail address: xujiaohh@163.com (J. Xu).

as the key factor for observing synergies in tar and gas compositions (Jones et al., 2005). Vacuum pyrolysis char, which has more “open” pore structure and is more reactive than atmospheric pyrolysis char (Ismadji et al., 2005), was expected to promote char gasification in this study. Low heating rate was employed during pyrolysis to facilitate “gas–lignite” interactions based on the different volatile release rates of lignite and biomass (Sonobe et al., 2008). And the high temperature was anticipated to benefit char gasification and secondary tar cracking (Krerkkaiwan et al., 2013; Zhong et al., 2012). Char, tar and gas were characterized with Brunauer–Emmitt–Teller (BET), gas chromatography–mass spectrometry (GC–MS) and gas chromatography (GC) techniques.

2. Methods

2.1. Experimental samples

Rice husk from rural area of Tianjin city and lignite from Neimeng Province, China were used in this study. The samples were ground to 0.13–0.18 mm and dried at 105 °C for 24 h. Rice husk and lignite were blended complying with the ratio of 1:1 in weight. The proximate and ultimate analyses were taken place in a tube furnace and Vario MACRO CHN/CHNS element analyzer respectively according to GB483-87 in China. Proximate and ultimate analyses of samples are listed in Table 1.

2.2. Experimental apparatus and procedure

All pyrolysis experiments were carried out on a fixed bed pyrolysis system. The inner size of the fixed bed reactor is 0.3 m × 0.3 m × 0.4 m (height). N₂ was used to purge air in the fixed bed reactor after samples were loaded, and then removed by a vacuum pump, providing a vacuum space for pyrolysis experiments. The initial total pressure in the reactor was around 5 kPa (–95 kPa). Final total pressures when pyrolysis processes ended were below 25 kPa (–75 kPa) according to actual experiments. The reactor was kept closed during the whole pyrolysis process. Approximately 10 g samples were used in each experiment. Each sample was heated from ambient temperature to desired temperature at a rate of 10 °C/min and kept at that temperature for 2 h. Experiment temperature in this study was 900 °C. Volatile products (tar and gas) were pumped out. The tar, condensed in traps and connecting pipelines, was recovered by washing with isopropanol as a solvent. A rotary evaporator was used to remove the solvent and water from tar which, afterwards, was weighed and collected. Non-condensable gas was measured by a cumulative volume flow meter and collected by gas bags. The char was collected and weighed when the temperature in the reactor was lower than 100 °C. Each experiment in this study was repeated three times.

Table 1
Proximate and ultimate analysis of samples.

Description	Lignite	Rice husk
<i>Ultimate analysis (dry basis)</i>		
Carbon (wt.%)	53.65	37.62
Hydrogen (wt.%)	4.12	4.91
Nitrogen (wt.%)	0.41	0.53
Sulfur (wt.%)	0.46	0.12
Oxygen (wt.%)	35.93	40.92
<i>Proximate analysis (dry basis)</i>		
Volatiles (wt.%)	56.98	66.82
Fixed carbon (wt.%)	37.59	17.28
Ash (wt.%)	5.43	15.90

2.3. Characterization

The nitrogen adsorption and desorption at 77.35 K using char samples were applied for BET analysis. Samples were degassed at 300 °C for 6 h before adsorption. The pyrolysis gas was analyzed by Agilent 7890A GC/TCD with a Molsieve 5A packed column (6 ft × 1/8″ × 2 mm). Chemical compounds of tar were analyzed by a GC–MS instrument (Agilent 6890 GC-5795C MS) with a HP-5MS capillary column (30 m × 0.25 mm × 0.25 μm). The oven temperature was programmed to hold at 50 °C for 3 min, ramp to 280 °C at 15 °C/min and hold at 280 °C for 5 min. The injector split ratio was set to 10:1, and the injector temperature was 300 °C. The flow rate of the He carrier gas was 1 mL/min.

2.4. Calculations

Average relative deviation between experimental value and calculated value was applied to analyze whether synergetic effect exists in the co-pyrolysis process. In this study, the blend ratio is a fixed value (1:1). The calculated values can be calculated by Eqs. (1)–(3):

$$Cal_{yield,i} = \frac{Y_{lignite,i} + Y_{biomass,i}}{2} \tag{1}$$

$$Cal_{mfra,m} = \frac{F_{Lgas,m} \times Y_{lignite,gas} + F_{biogas,m} \times Y_{biomass,gas}}{Y_{lignite,gas} + Y_{biomass,gas}} \tag{2}$$

$$Cal_{char,n} = \frac{E_{Lchar,n} \times Y_{lignite,char} + E_{biochar,n} \times Y_{biomass,char}}{Y_{lignite,char} + Y_{biomass,char}} \tag{3}$$

where $Cal_{yield,i}$ is the calculated yield (or volume yield) of i , including char, tar and gas. $Y_{lignite,i}$ and $Y_{biomass,i}$ are lignite and biomass experimental yields of i . $Cal_{mfra,m}$ is the calculated molar fraction of gas component m . $F_{Lgas,m}$ and $F_{biogas,m}$ are molar fractions of gas component m in lignite gas and biomass gas, respectively. $Y_{lignite,gas}$ and $Y_{biomass,gas}$ are experimental volume yields of lignite gas and biomass gas. $Cal_{char,n}$ is the calculated value of char's characteristic n , including volatiles content, fixed carbon content, ash content, BET surface area, pore volume and average pore size. $Y_{lignite,char}$ and $Y_{biomass,char}$ are experimental yields of lignite char and biomass char. $E_{Lchar,n}$ and $E_{biochar,n}$ are experimental values of lignite char's and biomass char's characteristic n . The average relative deviations can be calculated by Eq. (4):

$$\text{Average relative deviation} = \frac{|\text{Blend experimental value} - \text{Calculated value}|}{\text{Calculated value}} \times 100\% \tag{4}$$

3. Results and discussion

3.1. Product yields

The experimental and calculated product yields from the pyrolysis of lignite, rice husk and their blend are shown in Fig. 1a and b, respectively. Tar and char yields of the blend were lower than those of parent fuels and calculated values. The average relative deviations were 24.8% and 17.2%, respectively. The gas volume yield of the blend was obviously higher than that of both lignite and rice husk. The average relative deviation between the blend gas volume yield and calculated value was 24.5%. These results indicated remarkable synergetic effects during co-pyrolysis of lignite and rice husk. It was likely that the addition of biomass (rice husk) facilitated char gasification and secondary cracking of condensable compounds in tar, which, in further, led to the increase of gas yield and the decrease of tar and char yields.

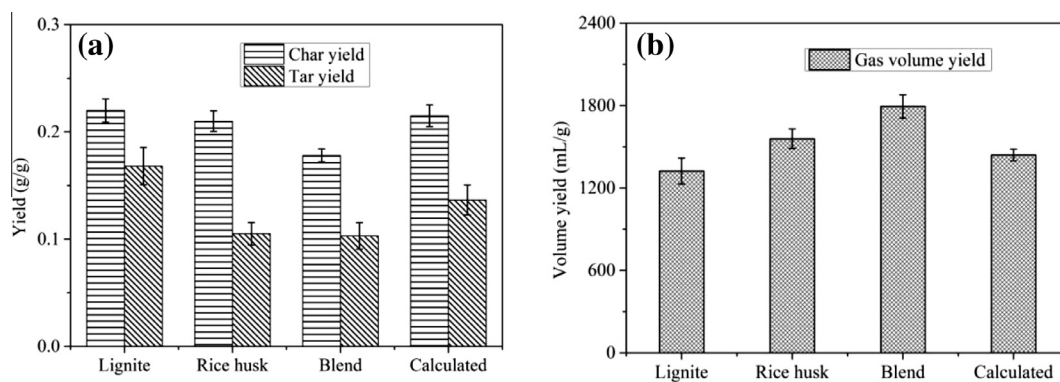


Fig. 1. (a) Char and tar yields; (b) gas volume yield.

3.2. Char analysis

Proximate analysis of chars was shown in Table 2. Fixed carbon and volatiles contained in blend char were lower than calculated values. The average relative deviations were 26.5% and 8.3%. The clearly reduction of fixed carbon might be the result of char gasification promoted by addition of biomass that provided more volatiles (CO_2 and H_2O) and catalysts (AAEM) during co-pyrolysis (Keown et al., 2008). This would also be a reasonable explanation for the decrease of char yield (Section 3.1). Besides, reduction of fixed carbon and volatile will inevitably improve the proportion of ash in blend char, which may invite changes of char structure.

Fig. 2 shows the nitrogen adsorption isotherms at 77.35 K for the resulting chars from pyrolysis of lignite, rice husk and their blend. Though they all resemble Type IV isotherms in BDDT (Brunauer–Deming–Deming–Teller) classification consisting of both micro and mesopores, great differences on BET surface area and pore volume were indicated. As shown in Table 2, the BET surface area and pore volume of rice husk char were approximately 56.3% and 40.0% of those of lignite char respectively. It could be attributed to that biomass (rice husk) released more volatiles causing the collapse of pore wall, and the alkali and alkaline earth metals (AAEM) in biomass might act as catalysts for char gasification destroying char structure largely (Kerckkaiwan et al., 2013; Keown et al., 2008). Besides, the present of AAEM can also result in the decrease of BET surface area by blocking pores of char (Carrier et al., 2012). While, interestingly, the adsorption isotherm, BET surface area and pore volume of blend char were similar to those of rice husk char and evidently different from those of lignite char and calculated value. Both BET surface area and pore volume of blend char were lower than calculated values. The average relative deviations were 26.3% and 40.1%, respectively. It was clear that the structure of blend char was influenced by synergistic

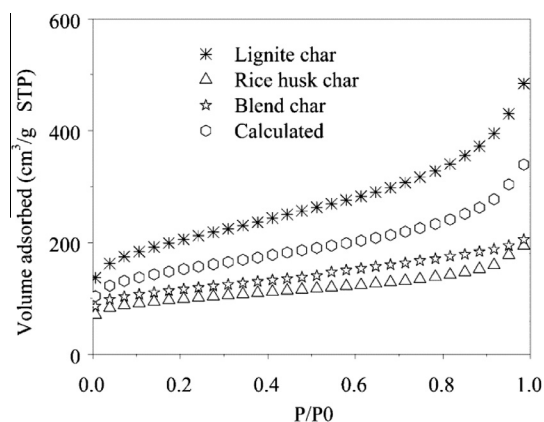


Fig. 2. Adsorption isotherms of chars.

effects under co-pyrolysis conditions in this study. There might be two possible explanations for the structure change of blend char. One was that the blend char structure was destroyed by intense char gasification discussed above. The other was the increased ash occupation that blocked the pores and reduced the BET surface area and pore volume of blend char, which was also agree with the smaller average pore size of blend char comparing with the calculated value (shown in Table 2).

3.3. Tar components

Table 3 shows the main components of lignite tar, rice husk tar and blend tar. Lignite tar mainly contained phenolics (3-(1H-1,2,3,4-tetrazol-5-yl)-1,2-benzenediol), alcohols (1,4-cyclohexanediol), aldehydes (octanal, furfural, benzaldehyde) and other heterocyclic compounds. Polycyclic aromatic hydrocarbons (PAHs), which were reported as main components in coal derived tar (Aboyade et al., 2013; Kerckkaiwan et al., 2013), were not detected in lignite tar in this study. It might be the high temperature (900 °C) and long contact time (more than 2 h) in this study that caused the cracking of PAHs, such as naphthalene, methyl naphthalene and anthracene. Rice husk tar, which was consistent with the reported results (Aboyade et al., 2013; Kerckkaiwan et al., 2013; Garcia-Perez et al., 2007), had a higher relative content of oxygenates such as acids (4-hydroxy-butanolic acid, propanoic acid, butanoic acid), furans (2(5H)-furanone), nitriles (acetonitrile) and ketones (3-pentanone, 3-methyl-2-cyclopenten-1-one, 3-methyl-2-butanone). Significant synergistic effects were found when comparing species of blend tar with those of lignite tar. Those main components of lignite tar, such as 3-(1H-1,2,3,4-tetra-

Table 2
Characteristics of chars.

Characteristics	Lignite char	Rice husk char	Blend char	Calculated value
<i>Proximate analysis</i>				
Moisture (wt.%)	–	–	–	–
Volatiles (wt.%)	25.63	7.50	15.38	16.78
Fixed carbon (wt.%)	49.73	16.79	24.73	33.64
Ash (wt.%)	24.64	75.71	59.89	49.58
<i>BET analysis</i>				
BET surface area (m^2/g)	726.07	408.66	420.77	571.05
Total pore volume (cm^3/g)	0.75	0.30	0.32	0.53
Average pore size (Å)	41.27	29.45	30.18	35.50

– not detected.

Table 3
Components of tars.

Lignite tar			Rice husk tar			Blend tar		
Species	Retention time (min)	Relative content ^a (%)	Species	Retention time (min)	Relative content ^a (%)	Species	Retention time (min)	Relative content ^a (%)
1,2-Benzenediol, 3-(1H-1,2,3,4-tetrazol-5-yl)-	8.837	24.84	Butanoic acid, 4-hydroxy-	6.881	30.03	Pentanoic acid, 4-oxo-	5.177	23.25
1,4-Cyclohexanediol, trans-Octanal	5.123 3.428	23.66 12.01	2(5H)-Furanone Acetonitrile, (dimethylamino)-	6.847 3.247	13.1 11.8	2-Pentanone, 4-hydroxy-4-methyl-	5.133 3.256	19.18 7.28
Pyridine	3.205	5.03	Propanoic acid	2.482	6.07	3-Pentanone	2.541	1.72
Furfural	4.880	4.91	3-Pentanone	2.539	2.5	Ethane, 1,1-diethoxy-	2.911	1.65
Acetonitrile, (dimethylamino)-	3.251	2.31	2-Cyclopenten-1-one, 3-methyl-	8.416	2.13	Ethylamine, 1-methyl-2-(5-methyl-1H-pyrazol-3-yl)-	39.427	1.62
Benzonitrile	8.987	2.10	2-Butanone, 3-methyl-	2.220	2	Ethylbenzene	5.590	1.48
2-Cyclopenten-1-one, 3-methyl-	8.589	1.93	Undecane	12.324	1.92	Propanoic acid	2.474	1.30
Butanoic acid, 4-hydroxy-	6.919	1.46	Ethylbenzene	5.594	1.87	Undecane	12.325	1.08
Benzaldehyde	8.366	1.28	Butanoic acid	3.773	1.81	Butanoic acid, 4-hydroxy-	6.932	1.04
Acetophenone	11.321	1.14	Ethane, 1,1-diethoxy-	2.908	1.56	2,2-Dimethoxybutane	3.376	0.87
Pyrazine, methyl-	4.721	1.06	2,2-Dimethoxybutane	3.373	1.23	Formamide, N,N-dimethyl-	4.027	0.55

^a GC/MS area percentage.

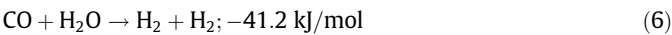
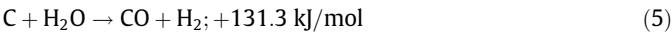
Table 4
Gas components' molar fractions, mol.%.

Gas components	Lignite gas	Rice husk gas	Blend gas	Calculated value
H ₂	22.50	25.78	25.32	24.27
CO ₂	13.15	31.79	27.62	23.22
CO	63.96	38.47	41.82	50.19
CH ₄	0.39	3.96	5.24	2.32

zol-5-yl)-1,2-benzenediol, trans-1,4-Cyclohexanediol, and octanal, were not detected in blend tar. It is highly possible that they were cracked when rice husk was added and pyrolyzed with lignite. More H₂ and catalysts provided by biomass (rice husk) might be the key factors resulting in the secondary cracking of those components in lignite tar during high temperature co-pyrolysis (Zhong et al., 2012; Strugnelli and Patrick, 1996). Simultaneously, the cracking process can produce more gas, such as CO, CO₂, CH₄ and H₂O, with the reduction of condensable tar yield. If so, it could also be considered as a possible explanation for the decrease of tar yield and increase of gas yield (Section 3.1).

3.4. Gas composition

Table 4 shows compositions of gases derived from pyrolysis of lignite, rice husk and their blend. The average relative deviations between blend gas components' molar fractions and calculated values were 4.3%, 19.0%, 16.7%, and 125.9% for H₂, CO₂, CO and CH₄, respectively. The CH₄ molar fraction had the largest average relative deviation, whereas it can hardly be a convincing evidence for synergetic effects due to the low molar fraction of CH₄. However, the average relative deviations between H₂, CO₂ and CO molar fractions and calculated values indicated some synergetic effects on gaseous phase interactions. Molar fractions of H₂ and CO₂ in blend gas were higher than calculated values, while CO molar fraction was evidently lower than the calculated value. It was probably that more H₂O produced by biomass pyrolysis facilitated both the char-water gasification and water–gas shift reaction (Li and Suzuki, 2010), expressed as Eqs. (5) and (6):



4. Conclusion

Special experimental conditions (vacuum reactor, long contact time, high temperature and low heating rate) were employed to observe synergetic effects during co-pyrolysis of lignite and biomass (rice husk) in this study. Remarkable synergetic effects were observed. Addition of biomass obviously influenced the tar and char yields, gas volume yield, gas composition, char structure and tar composition during co-pyrolysis by promoting char gasification, gaseous phase interactions, and secondary tar cracking.

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References

Aboyade, A.O., Carrier, M., Meyer, E.L., et al., 2013. Slow and pressurized co-pyrolysis of coal and agricultural residues. *Energy Convers. Manage.* 65, 198–207.
Carrier, M., Hardie, A.G., Uras, U., et al., 2012. Production of char from vacuum pyrolysis of South-African sugar cane bagasse and its characterization as activated carbon and biochar. *J. Anal. Appl. Pyrolysis* 96, 24–32.

- Garcia-Perez, M., Chaala, A., Pakdel, H., et al., 2007. Vacuum pyrolysis of softwood and hardwood biomass: comparison between product yields and bio-oil properties. *J. Anal. Appl. Pyrolysis* 78, 104–116.
- Haykiri-Acma, H., Yaman, S., 2010. Interaction between biomass and different rank coals during co-pyrolysis. *Renew. Energy* 35, 288–292.
- Idris, S.S., Rahman, N.A., Ismail, K., et al., 2010. Investigation on thermochemical behavior of low rank Malaysian coal, oil palm biomass and their blends during pyrolysis via thermogravimetric analysis (TGA). *Bioresour. Technol.* 101, 4584–4592.
- Ismadji, S., Sudaryanto, Y., Hartono, S.B., et al., 2005. Activated carbon from char obtained from vacuum pyrolysis of teak sawdust: pore structure development and characterization. *Bioresour. Technol.* 92, 1364–1369.
- Jones, J.M., Kubacki, M., Kubica, K., et al., 2005. Devolatilisation characteristics of coal and biomass blends. *J. Anal. Appl. Pyrolysis* 74, 502–511.
- Keown, D.M., Hayashi, J., Li, C., 2008. Effects of volatile-char interactions on the volatilization of alkali and alkaline earth metallic species during the pyrolysis of biomass. *Fuel* 87, 1187–1194.
- Krerkkaiwan, S., Fushimi, C., Tsutsumi, A., et al., 2013. Synergetic effect during co-pyrolysis/gasification of biomass and sub-bituminous coal. *Fuel Process. Technol.* 115, 11–18.
- Li, C., Suzuki, K., 2010. Process design and simulation of H₂-rich gases production from biomass pyrolysis process. *Bioresour. Technol.* 101, S86–S90.
- Li, S., Chen, X., Wang, L., et al., 2013. Co-pyrolysis behaviors of saw dust and shenfu coal in drop tube furnace and fixed bed reactor. *Bioresour. Technol.* 148, 24–29.
- Li, S., Chen, X., Liu, A., et al., 2014. Study on co-pyrolysis characteristics of rice straw and Shenfu bituminous coal blends in a fixed bed reactor. *Bioresour. Technol.* 155, 252–257.
- Meesri, C., Moghtaderi, B., 2002. Lack of synergetic effects in the pyrolytic characteristics of woody biomass/coal blends under low and high heating rate regimes. *Biomass Bioenergy* 23, 55–66.
- Park, D.K., Kim, S.D., Lee, S.H., et al., 2010. Co-pyrolysis characteristics of sawdust and coal blend in TGA and a fixed bed reactor. *Bioresour. Technol.* 101, 6151–6156.
- Sadhukhan, A.K., Gupta, P., Goyal, T., et al., 2008. Modelling of pyrolysis of coal-biomass blends using thermogravimetric analysis. *Bioresour. Technol.* 99, 8022–8026.
- Sonobe, T., Worasuwannarak, N., Pipatmanomai, S., 2008. Synergies in co-pyrolysis of Thai lignite and corncob. *Fuel Process. Technol.* 89, 1371–1378.
- Strugnelli, B., Patrick, J.W., 1996. Rapid hydrolysis studies on coal and maceral concentrates. *Fuel* 75, 300–306.
- Vassilev, S.V., Baxter, D., Andersen, L.K., et al., 2010. An overview of the chemical composition of biomass. *Fuel* 89, 913–933.
- Veraa, M.J., Bell, A.T., 1978. Effect of alkali metal catalysts on gasification of coal char. *Fuel* 57, 194–200.
- Vuthaluru, H.B., 2004. Investigations into the pyrolytic behavior of coal/biomass blends using thermogravimetric analysis. *Bioresour. Technol.* 92, 187–195.
- Weiland, N.T., Means, N.C., Morreale, B.D., 2012. Product distributions from isothermal co-pyrolysis of coal and biomass. *Fuel* 94, 563–570.
- Zhang, L., Xu, S., Zhao, W., et al., 2007. Co-pyrolysis of biomass and coal in a free fall reactor. *Fuel* 86, 353–359.
- Zhong, M., Zhang, Z., Zhou, Q., et al., 2012. Continuous high-temperature fluidized bed pyrolysis of coal in complex atmospheres: product distribution and pyrolysis gas. *J. Anal. Appl. Pyrolysis* 97, 123–129.